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# Applications of Spectral-Representation Model as a Potential Method for Cu Clusters

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## ABSTRACT

We applied the spectral-representation technique developed by Katsuki and Huzinaga as a model potential in calculating the electronic structure of Cu clusters. The characteristics of this potential were closely investigated in Cu and Cu<sub>2</sub>. For Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, and Cu<sub>13</sub>, we performed all-electron *ab initio* self-consistent field calculations and model-potential calculations where 3*p*, 3*d*, and 4*s* electrons, and 3*d* and 4*s* electrons are treated as valence electrons. The ionization potentials (IPs) given by the all-electron calculations were 6.26, 5.55, 4.52, 4.02, and 4.08 eV for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, and Cu<sub>13</sub>, respectively. The IPs given by the model-potential calculations were 6.25, 5.56, 4.62, 4.09, and 4.23 eV for the 3*p*-, 3*d*-, and 4*s*-valence electrons, and 6.26, 5.68, 4.71, 4.07, and 4.19 eV for the 3*d*- and 4*s*-valence electrons. The IPs given by the model-potential calculations agree well with those of the all-electron calculations. We also performed model-potential calculations where only the 4*s* electrons were treated as valence electrons. The calculated IPs were 6.47, 5.98, 5.38, 4.63, and 4.88 eV for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, and Cu<sub>13</sub>, respectively. These are ca. 0.8 eV higher than the IPs by the all-electron calculation for the larger clusters of Cu<sub>5</sub>, Cu<sub>9</sub>, and Cu<sub>13</sub>. The higher IPs originate from the expulsion of the 3*d* electrons from the valence electrons. We also performed model-potential calculations with 4*s* electrons for Cu<sub>74</sub>. The calculated IP is 4.61 eV, which is estimated to be 0.8 eV larger than that obtained by the all-electron calculation. The IPs with correlation corrections are 7.7, 7.4, 6.3, 5.8, 5.9, and 5.6 eV for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, Cu<sub>13</sub>, and Cu<sub>74</sub>.

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respectively. Experimental values are 7.73, 7.37, 6.30, 5.37, 5.67, and 5.26 eV. The agreement between the two is fairly good. The electron affinities are also discussed. © 1996 by John Wiley & Sons, Inc.

## Introduction

One of the most serious problems in molecular electronic calculations is the increase of molecular integrals when to handling larger systems. To solve the problem, many types of effective core potentials<sup>1-4</sup> and model potentials<sup>5-7</sup> have been introduced. The common characteristic of all the effective core and model potentials is that they require parameters which describe the potentials or atomic orbitals. It requires experience and skill to determine the parameters. Recently Katsuki and Huzinaga<sup>8,9</sup> developed a spectral-representation model potential which needs no such parameters. The technique may be summarized thus.

In the Hartree-Fock (HF) approximation, the equation to be solved is

$$F\varphi_i = \varepsilon\varphi_i \quad (1)$$

where  $F$  is the Fock operator and  $\varphi_i$  is the eigenfunction. For the closed shell problems, it takes the form of

$$F = -\frac{1}{2}\Delta - \sum_a Z_a/r_a + \sum_j (2J_j - K_j) \quad (2)$$

where

$$J_i f(1) = \int dv_2 \varphi_i^*(2) \varphi_i(2) (1/r_{12}) f(1) \quad (3)$$

and

$$K_j f(1) = \int dv_2 \varphi_j^*(2) f(2) (1/r_{12}) \varphi_j(1). \quad (4)$$

In eq. (2),  $a$  indicates the  $a$ th atom which constitutes a molecule, and  $j$  indicates  $j$ th molecular orbitals  $\varphi_j$ . Introducing a complete set  $\{\chi_p\}$ , we can rewrite the Fock operator as

$$F = -\frac{1}{2}\Delta + \left[ -\sum_a Z_a/r_a + \sum_j^{\text{val}} (2J_j - K_j) - V_{\text{ad}} \right] + V_{\text{eff}} \quad (5)$$

where

$$V_{\text{eff}} = \Omega \left[ \sum_j^{\text{frozen}} (2J_j - K_j) + V_{\text{ad}} \right] \Omega, \quad (6)$$

$$\Omega = \sum_{pq} |\chi_p\rangle (S^{-1})_{pq} \langle \chi_q|, \quad (7)$$

and

$$S_{pq} = \langle \chi_p | \chi_q \rangle. \quad (8)$$

The operator  $\Omega O \Omega$  is called the spectral representation of the operator  $O$ . If we use eq. (5) instead of eq. (2), we should add a shift operator constructed from the frozen orbitals  $\varphi_j$  and their orbital energies  $\varepsilon_j$ .

$$P = \sum_j^{\text{frozen}} 2\varepsilon_j |\varphi_j\rangle \langle \varphi_j|. \quad (9)$$

Under the frozen core approximation irrespective of the form of  $V_{\text{ad}}$ , eq. (5) yields accurate results so far as the function set  $\{\chi\}$  is complete. Here, we take  $V_{\text{ad}}$  to be equal to  $-Z_a^c/r_a$  where  $Z_a^c$  is the number of core electrons in the  $a$ th atom.

For a molecular system, the Fock operator can be expressed as follows:

$$F = -\frac{1}{2}\Delta + \left[ -\sum_a Z_a/r_a + \sum_j^{\text{val}} (2J_j - K_j) - \left( \sum_a -Z_a^c/r_a \right) \right] + \sum_a V_{\text{eff}}^a + \sum_a P^a \quad (10)$$

where  $V_{\text{eff}}^a$  is given by

$$V_{\text{eff}}^a = \Omega^a \left[ -Z_a^c/r_a + \sum_j^{\text{frozen}} (2J_j^a - K_j^a) \right] \Omega^a \quad (11)$$

with

$$\Omega^a = \sum_{pq} |\chi_p^a\rangle (S^{-1})_{pq}^a \langle \chi_q^a|, \quad (12)$$

$$S_{pq}^a = \langle \chi_p^a | \chi_q^a \rangle, \quad (13)$$

and

$$P^a = - \sum_j^{\text{frozen}} 2\varepsilon_j^a |\varphi_j^a\rangle \langle \varphi_j^a|. \quad (14)$$

The present model potential obtained by the use of the spectral-representation technique has several distinctive characteristics. First, the present model potential can be obtained straightforwardly without any adjusting and/or fitting process from the function set  $\{\chi^a\}$ , the set of the frozen-core orbitals  $\{\varphi_j^a\}$ , and their orbital energies  $\{\varepsilon_j^a\}$ . Therefore, anyone can prepare a model potential suitable to his/her particular requirements. Second, the  $V_{\text{ad}}$  in eq. (6) is not necessarily spherically symmetric as the usual model potentials tacitly assume. One can freeze nonspherical electron density such as the electron occupying the inactive molecular orbitals of the functional groups such as COOH.<sup>9</sup> Third, the only evaluation which is needed to incorporate the model potential into the molecular orbital calculations is the overlap integral between the valence-orbital basis functions and the function set  $\{\chi^a\}$ . Therefore, once the model potentials have been prepared and stored in a file, the computing time is negligibly short. Fourth, the fact that the necessary calculations are overlap-integral evaluations makes the present model potential suitable to the energy gradient method. Hereafter, we call  $V_{\text{eff}}^a + P^a$  in eq. (10) an atomic model potential or simply a model potential of the  $a$ th atom. In the next section we describe the results of testing several sets of  $\{\chi^a\}$  and  $\{\varepsilon_j, \varphi_j^a\}$  for the Cu atom and the Cu<sub>2</sub> molecule, changing the valence basis sets.

Using the model potentials discussed above and the basis set selected, we will investigate the ionization potentials (IPs) and electron affinities (EAs) of Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, Cu<sub>13</sub>, and Cu<sub>74</sub> for which the precise experimental values<sup>10-12</sup> are given, with the sole exception of EA for Cu<sub>74</sub>.

Before closing this section, a comment is necessary on the inverse overlap matrix of  $S^{-1}$  which appears in eqs. (7) and (12). One may suspect the divergence of  $S^{-1}$  in these equations which might be brought by the linear dependence in the employed basis set. It is, we believe, quite safe from the divergence so far as similar exponents of the primitive Gaussian-type functions (pGTFs) are not used in the basis set, because  $S^{-1}$  is calculated over the pGTFs which span the separate spaces of the  $s$ ,  $p$ , and  $d$  symmetries of the respective atoms. Actually we did not meet the difficulty in any size of the clusters when we used the large set for eq.

(12) composed of 20  $s$ -, 14  $p$ -, and 10  $d$ -type pGTFs.

## Application to Cu Atom

To determine whether the present model potential discussed can approximate the electronic structure obtained by the all-electron calculation with high *fidelity*, we first applied the model potential to the IP calculations for the Cu atom. We used the common basis sets for the valence orbital calculations (entries c, d, and e) and for the all-electron calculation (entry a) as shown in Table I. We use two symbols (././.) and [.../.../...] which denote a primitive and a contracted Gaussian type function (cGTF) basis set, respectively. The slashes separate the  $s$ ,  $p$ , and  $d$  symmetries and the polarization function is indicated by an asterisk (\*). The valence-orbital basis set used to check the fidelity of the model potential is [43321/1\*/41] for the  $sd$  valence orbital calculations. The basis set for the reference all-electron calculations is [43321/431\*/41]. These basis sets are derived from the method of Tatewaki et al.<sup>13,14</sup> (see also Table II).

To solve the HF equation for  $F$  defined by eq. (10), we used the basis sets for the spectral representation  $\Omega^a$ , and the core orbitals  $\{\varphi_j\}$  for the projection operator  $P^a$ , and the Coulomb and exchange operators, besides the basis sets for the valence orbitals. The first three model potentials given in the entries c, d, and e of Table I are specified by the basis set for the spectral representation and the orbitals for the frozen core. The IPs given in entries c, d, and e are almost the same within each state, which shows that the IPs are independent of the basis sets for  $\Omega^a$  and the core orbitals  $\{\varphi_j\}$ . Note that the IPs obtained with the use of the model potentials are very close to the IPs obtained by the all-electron calculation. These results indicate that the model potential can approximate the all-electron results with very high fidelity. We used the [43321/1\*/41] basis set for the valence orbitals as a fidelity check. The [43321/1\*/41] basis set is too large in practice to calculate the electronic structure for large systems such as the Cu<sub>74</sub> cluster.

Next, we calculate the IPs of the Cu atom using a much smaller basis set for the valence orbitals. Seijo, Barandiaran, and Huzinaga (SBH)<sup>7</sup> obtained *ab initio* model potentials where the local Coulomb operators of the *ab initio* model potentials are mapped to the model functions

**TABLE I.**  
**Energy Levels of Cu Atom.**

All-Electron Calculations			Ionization Potentials (eV)		
			$^1S$	$^3D$	$^1D$
(a) [43321 / 431* / 41] <sup>a</sup> $\equiv$ G			6.26	7.74	8.08
(b) [566666111 / 4551111,1* / 61111] <sup>b</sup>			6.41	7.67	8.08
Model-Potential Calculations					
Basis Set for Valence Electrons	Basis Set for $\Omega$ in eq. (12)	Core Orbitals for $\varphi_j \rangle \langle \varphi_j$ , eq. (14)			
(c) [43321 / 1* / 41] <sup>a</sup>	All pGTFs in G	1s, 2s, 3s, 2p, 3p given by G	6.26	7.71	8.06
(d) [43321 / 1* / 41] <sup>a</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p given by G	6.26	7.71	8.06
(e) [43321 / 1* / 41] <sup>a</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p by (20 / 13 / 10)	6.27	7.68	8.03
(f) [81 / 1* / 41] <sup>c</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p by (20 / 13 / 10)	6.26	8.46	8.72
(g) [81 / 51* / 41] <sup>c</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p by (20 / 13 / 10)	6.25	8.46	8.72
(h) [711 / 1* / 41] <sup>c</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p by (20 / 13 / 10)	6.26	7.66	8.03

<sup>a</sup>The cGTFs generated from [4333 / 43 / 5] set given in ref. 14 plus one *p*-type polarization function.<sup>b</sup>The cGTF set generated from (20 / 13 / 10) given in ref. 15 plus one *p*-type polarization function.<sup>c</sup>The basis set generated from (9 / 5 / 5) given in ref. 7 plus one *p*-type polarization function.

$\{\sum_k A_k \exp(-\alpha_k r^2)/r\}$  and nonlocal exchange operators are expressed in the spectral-representation form. The valence-orbital basis sets are optimized by minimizing the valence self-consistent field (SCF) energy using their model potentials. If the fitting for the Coulomb operator is perfect and the basis sets for the spectral representation are complete, then the *ab initio* model potential and our model potential should have the same effects on the valence orbitals. Both methods produce valence orbitals with nodes which compare favorably to those orbitals of HF. Therefore, the valence-orbital basis sets obtained by the *ab initio* model potentials<sup>7</sup> should be suitable basis sets for our model potentials. We borrowed their (9/5/5) valence orbital basis set for Cu, contracting it as [81/51\*/41], [81/1\*/41], and [711/1\*/41], where 1\* stands for the polarization function used above. The first seven of nine *s*-type pGTFs for the 4s orbital are used for the orthogonalization to 1s, 2s, and 3s orbitals. The [711/1\*/41] set is the most relaxed one among the three sets for the 4s orbital. The respective basis sets for the  $\Omega^a$  and  $P^a$  are (20/13,1\*/10) and (20/13/10; see ref. 15) in these three calculations. The *ab initio* model potential

has been aimed at getting results comparable to those at the level of the HF limit. For purposes of comparison, we calculated the IPs using the (20/13/10) well-tempered basis set contracted as [566666111/4551111\*/61111]. We listed the results in Table I, entry b. There is not much difference between the two all-electron results so far as the atomic calculations are concerned.

The 3d IPs given by the [81/51\*/41] and [81/1\*/41] sets are almost the same (Table I, entries f and g) and they are  $\sim 0.7$  eV larger than those of the reference all-electron calculations a and b. The [711/1\*/41] set provided excellent results for 3d IPs as well as 4s IP (Table I, entry h). Thus, the 3d–4s interaction is important for the 3d IP calculations. The inclusion of the 3p–3d interactions, on the other hand, is unimportant for obtaining the appropriate 3d IPs. The unimportance of the 3p–3d interactions is also shown in the calculations of Table I c, d, and e entries by comparing them with the result in the a entry: we note that no 3p orbitals are employed in c, d, and e. In the [43321/1\*/41] and [43321/431\*/41] sets three *s*-type cGTFs are used for the inner region, two cGTFs are used for the outer region of the 4s

**TABLE II.**  
**cGTF (4333 / 43 / 5) and Polarization Function for Cu.**

Orb Sym	1s	2s	3s	4s
Orb E	-328.244	-40.7484	-4.98105	-0.23090
$\langle r - 2 \rangle$	1609.43	157.460	22.8509	0.77009
$\langle r - 1 \rangle$	28.4772	6.22025	1.94446	0.37520
$\langle r - 1 \rangle$	0.05286	0.23770	0.72355	3.38934
$\langle r - 2 \rangle$	0.00377	0.06659	0.60488	13.5410
$r_{\max}$	0.03440	0.19880	0.62237	2.63023
c1	0.98981	0.33449	0.12597	-0.02182
c2	0.03357	-1.04029	-0.46122	0.07131
c3	0.00766	0.01279	-1.08754	0.24942
c4	0.00111	0.00076	0.00395	1.02553
Basis	s1	s2	s3	s4
e1	12089.304	166.95803	13.814849	0.88752228
e2	1823.5302	18.483882	2.2257608	0.10710259
e3	413.53596	7.6641691	0.85906487	0.03799219
e4	111.29899			
d1	0.0173351	-0.1082132	0.2248336	-0.0978264
d2	0.1214047	0.6401603	-0.7214133	0.5200087
d3	0.4402931	0.4321033	-0.4124074	0.5616982
d4	0.5542714			
Orb Sym	2p	3p	3d	
Orb E	-35.5545	-3.29628	-0.46752	
$\langle r - 3 \rangle$	656.313	83.1885	7.38984	
$\langle r - 2 \rangle$	51.6011	7.26648	2.69782	
$\langle r - 1 \rangle$	6.15525	1.81354	1.39401	
$\langle r - 1 \rangle$	0.20739	0.75806	0.97680	
$\langle r - 2 \rangle$	0.05270	0.67883	1.25990	
$r_{\max}$	0.15824	0.62590	0.63412	
c1	0.98929	-0.40366	1.00000	
c2	0.02933	1.06807		
Basis	p1	p2	d1	
e1	498.58239	0.73410312	47.886771	
e2	116.54226	5.3273781	13.346022	
e3	35.825982	2.0161455	4.4377998	
e4	12.057314		1.4365512	
e5			0.39445901	
d1	0.0282436	0.2498044	0.0317015	
d2	0.1824069	0.3174630	0.1651675	
d3	0.5072951	0.5574896	0.3819468	
d4	0.4548585		0.4630582	
d5			0.3278561	

Polarization function: 2p with exponent 0.090. We give the cGTF set of (4333 / 43 / 5) and the polarization function for Cu<sup>2</sup>S because ref. 14 is almost out of print. Total energy is -1637.427869. The symbols *si*, *pi*, and *di* represent the cGTFs of the *s*, *p*, and *d* symmetries. The *ei* and *di* represent the exponent parameters and contraction coefficients of the respective cGTFs. The symbols *is*, *ip*, and *id* show the atomic SCF orbitals whose expansion coefficients are *ci*.

**TABLE III.**  
**Spectroscopic Constants of Cu<sub>2</sub> by Various Environmental Potentials.**

			Spectroscopic Constants		
All-Electron Calculations			$R_e$ (au)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
(a) [43321 / 431* / 41] <sup>a</sup> $\equiv$ G			4.570	187.2	0.624
(b) [566666111 / 4551111, 1* / 61111] <sup>b</sup>			4.619	185.4	0.487
Model-Potential Calculations					
Basis for Valence Electrons	Basis for $\Omega$ in eq. (12)	Core Orbitals for $\varphi_j \rangle \langle \varphi_j$ , eq. (14)			
(c) [43321 / 1* / 41] <sup>a</sup>	All pGTFs in G	1s, 2s, 3s, 2p, 3p given by G	4.698	176.7	0.452
(d) [43321 / 1* / 41] <sup>a</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p given by G	4.584	203.7	0.566
(e) [43321 / 1* / 41] <sup>a</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p by (20 / 13 / 10)	4.600	201.2	0.532
(f) [81 / 1* / 41] <sup>c</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p by (20 / 13 / 10)	4.641	186.2	0.405
(g) [81 / 51* / 41] <sup>c</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p by (20 / 13 / 10)	4.451	178.5	0.580
(h) [711 / 1* / 41] <sup>c</sup>	(20 / 13, 1* / 10) <sup>b</sup>	1s, 2s, 3s, 2p, 3p by (20 / 13 / 10)	4.610	201.4	0.520

<sup>a</sup>The cGTFs generated from [4333 / 43 / 5] set given in ref. 14 plus one *p*-type polarization function.<sup>b</sup>The cGTF set generated from (20 / 13 / 10) given in ref. 15 plus one *p*-type polarization function.<sup>c</sup>The basis set generated from (9 / 5 / 5) given in ref. 7 plus one *p*-type polarization function.

orbital, and in the [711/1\*/41] set only one cGTF is used for the inner region and two cGTFs are used for the outer region of the same orbital. We can thus reduce the size of the valence orbital without deteriorating the quality under the model-potential method.

At the end of this section, we will comment on the basis-set dependence of the results obtained by using the basis sets [81/51\*/41], [81/1\*/41], and [711/1\*/41]. The basis-set dependence seen in Table I is not brought about by inadequacy of the model potential. The results reflect the different quality of the valence-orbital basis sets faithfully as often occurs in the all-electron calculations.

### Application to Cu<sub>2</sub> Molecule

The electronic structures of the Cu<sub>2</sub> molecule were calculated by the same method using the same basis sets used for calculations of the Cu atom. The calculated spectroscopic constants and the IPs are presented in Tables III and IV, respectively. The calculations a, c, d, and e were done to check the fidelity of the model potential as was done in the preceding section.

### SPECTROSCOPIC CONSTANTS

The two all-electron calculations (Table III, entries a and b) show that using the smaller basis set gives a smaller equilibrium bond distance ( $R_e$ ) and a larger dissociation energy ( $D_e$ ), due to basis-set superposition error (BSSE).<sup>16–19</sup> Because in the model-potential calculations the core electrons are assumed to create only the potentials, the BSSE from them should be zero. Consequently, the  $R_e$  given by the model-potential calculations is expected to be larger than that given by the Table III all-electron calculation a and the  $D_e$  given by the model potential is expected to be smaller than that of a. The results given in c, d, e, and h are in line with this speculation. The differences between c and {d, e, and h} are not so small, which shows that near completeness of the basis set in  $\Omega^a$  is necessary. The smaller differences between d and {e and h} arise from the differences in the atomic core orbitals for the integrals in eq. (11) and for the projection operator  $P^a$  in eq. (14). The results given by e and h are almost the same, indicating that the two valence basis sets [43321/1\*/41] and [711/1\*/41] are almost equivalent. Finally we comment that the spectroscopic constants given by

**TABLE IV.**  
**Ionization Potentials by Koopman's Theorem and  $\Delta$ SCF of  $\text{Cu}_2$ .**

Results of Symmetry Constrained SCF (eV)												
	$3d\sigma_u$		$3d\pi_g$		$3d\pi_u$		$3d\delta_u$		$3d\delta_g$		$4s\sigma_g$	
	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF
All-electron calculations												
(a)	12.12	9.27	12.35	9.44	12.82	10.01	12.56	9.74	12.63	9.82	5.94	5.55
(b)	12.61	9.38	12.79	9.53	13.28	10.17	13.00	9.87	13.08	9.99	6.13	5.66
Model-potential calculations												
(c)	12.23	9.41	12.51	9.61	13.05	10.26	12.73	9.92	12.81	10.02	5.95	5.65
(d)	12.32	9.51	12.57	9.67	13.05	10.26	12.75	9.96	12.82	10.04	5.98	5.68
(e)	12.30	9.50	12.56	9.66	13.04	10.25	12.74	9.95	12.81	10.03	5.98	5.69
(f)	11.99	9.57	12.21	9.81	12.69	10.37	12.41	10.01	12.48	10.09	5.84	5.63
(g)	11.73	9.22	11.92	9.46	12.39	10.00	12.15	9.68	12.21	9.76	5.76	5.44
(h)	12.34	9.52	12.60	9.76	13.08	10.32	12.78	9.96	12.85	10.04	5.98	5.68
Results of Symmetry Broken SCF (eV)												
	$3d\sigma_2$		$3d\sigma_1$		$3d\pi_2$		$3d\pi_1$		$3d\delta_2$		$3d\delta_1$	
	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF	kpmns	$\Delta$ SCF
All-electron calculations												
(a)	12.93	6.19	12.21	6.19	12.35	6.20	12.82	6.20	12.56	6.17	12.63	6.17
(b)	13.44	6.14	12.61	6.14	12.79	6.20	13.28	6.20	13.00	6.15	13.08	6.15
Model-potential calculations												
(c)	13.17	6.30	12.23	6.30	12.51	6.35	13.05	6.35	12.73	6.26	12.81	6.26
(d)	13.17	6.38	12.32	6.38	12.57	6.38	13.05	6.38	12.75	6.30	12.82	6.30
(e)	13.15	6.37	12.30	6.37	12.56	6.34	13.04	6.34	12.74	6.28	12.81	6.28
(f)	12.85	6.76	11.99	6.76	12.21	6.78	12.69	6.78	12.41	6.71	12.48	6.71
(g)	12.55	6.42	11.73	6.42	11.92	6.47	12.39	6.47	12.15	6.42	12.21	6.42
(h)	13.19	6.36	12.34	6.36	12.60	6.36	13.08	6.36	12.78	6.27	12.85	6.27

Calculations were performed at the bond distance of 4.83 au.

f are close to those of c and that the inclusion of the  $3p$ -like electrons (see g) into the valence ones exaggerates  $D_e$  a little.

### IPs

The IPs were calculated, not at the equilibrium nuclear distance, but at the bond distance (4.83 au) of the nearest neighbor in the solid. In the symmetry-constrained ( $D_{\infty h}$  symmetry), all-electron SCF calculations, the orbital energies of the larger set for the  $d$ -like orbitals (Table IV, entry b) are lower than those of the smaller basis set (Table IV, entry a) by ca. 0.5 eV. All the  $3d$  IPs calculated by  $\Delta$ SCF are smaller than those obtained by the Koopmans' theorem by ca. 3 eV. The reorganization energy is so large, we had to use  $\Delta$ SCF in calculating  $3d$  IPs. The differences in IPs between the two all-electron calculations a and b became only 0.1 eV in the  $\Delta$ SCF calculations. Basis a is sufficient to calculate

IPs. The results in c, d, e, and h are almost the same as each other, and their IPs in  $\Delta$ SCF for  $d$ -like electrons are larger than those of a by 0.2 eV. The differences between the model-potential IPs and the all-electron IPs of b become smaller (within  $\sim 0.1$  eV), but this does not indicate that the model-potential calculations give more accurate results than the all-electron calculation of a. The results of the model-potential calculations {c, d, and e} should agree with those of the a calculation, so far as the frozen core approximation is valid. In the symmetry-constrained  $\Delta$ SCF calculations, we did not see large differences between {c, d, e, and h} and f as we do in the atomic  $3d$  IPs. The results of  $\Delta$ SCF given in g are quite close to those given by a, which indicates that if the  $3d$  hole is delocalized, the  $3p$ - $3d$  mixture is important. This is the reason why the  $3d$  IPs given by {c, d, e, and h} and f which disregard the  $3p$  orbitals are different from those of a.

In the symmetry broken SCF ( $C_{\infty v}$ ), the calculated  $3d$  hole is strongly localized at one of the two atoms which constitute the  $\text{Cu}_2$  molecule; total energies calculated with the symmetry broken SCF are more stable (by ca. 3 eV) than those of the symmetry-constrained SCF ( $D_{\infty h}$ ). The atomic ionization process is predominant in the  $d$ -like electron ionization, a step which is widely known in transition metal clusters and solids.<sup>20–27</sup> Clear differences between Table IV entries {c, d, e, and h} and f are observed as they are in the Cu atom. The differences between {c, d, e, and h} and g are smaller than those between {c, d, e, and h} and f, probably because the  $p$  orbitals of the other atom are used to describe the hole state of the Cu atom under consideration.

## Application to Larger Clusters

### ORBITAL ENERGY DISTRIBUTIONS

The calculated orbital energies for Cu,  $\text{Cu}_2$ ,  $\text{Cu}_5$ ,  $\text{Cu}_9$ ,  $\text{Cu}_{13}$ , and  $\text{Cu}_{74}$  are summarized in Table V. The geometrical structures for  $\text{Cu}_5$ ,  $\text{Cu}_9$ ,  $\text{Cu}_{13}$ , and  $\text{Cu}_{74}$  are the pyramid ( $\text{Cu}_1\text{--Cu}_4\text{:C}_{4v}$ ), the square antiprism ( $\text{Cu}_4\text{--Cu}_5\text{:C}_{4v}$ ), the cubo-octahedron ( $\text{Cu}_4\text{--Cu}_5\text{--Cu}_4\text{:O}_h$ ), and the rectangular parallelepiped ( $\text{Cu}_{25}\text{--Cu}_{24}\text{--Cu}_{25}\text{:D}_{4h}$ ). The bond length (4.83 au) of the nearest neighbor is that of the solid. The all-electron calculations were performed for Cu,  $\text{Cu}_2$ ,  $\text{Cu}_5$ ,  $\text{Cu}_9$ , and  $\text{Cu}_{13}$  using the [43321/431\*/41] basis set. For the model-potential calculations we used the basis set made

**TABLE V.**  
Distribution of Orbital Energies by Various Numbers of Valence Electrons.

	All Electron	Model Potential			
	29 <sup>a</sup> [43321 / 431* / 41]	17 <sup>a</sup> [711 / 51* / 41]	11 <sup>a</sup> [711 / 1* / 41]	11 <sup>a</sup> [711 / 0 / 41]	1 <sup>a</sup> [711 / 0 / 0]
Orbital Energies for lowest 4s-like orbitals (eV)					
$\text{Cu}_1(^2S)$	6.29	6.27	6.29	6.29	6.47
$\text{Cu}_2(^1\Sigma_g^+)$	5.94	5.94	5.98	5.96	6.16
$\text{Cu}_5(^4A_2)^b$	9.23	9.29	9.44	9.50	10.01
$\text{Cu}_9(^2B_2)$	10.80	10.93	11.59	11.74	12.66
$\text{Cu}_{13}(^6A_{1g})^c$	12.26	12.36	13.61	13.79	15.35
$\text{Cu}_{74}(^1A_{1g})$				—	21.04
Orbital energies for highest 4s-like orbitals (eV)					
$\text{Cu}_1(^2S)$	6.29	6.27	6.29	6.29	6.47
$\text{Cu}_2(^1\Sigma_g^+)$	5.94	5.94	5.98	5.96	6.16
$\text{Cu}_5(^4A_2)^b$	4.81	4.92	5.00	4.99	5.54
$\text{Cu}_9(^2B_2)$	4.26	4.33	4.27	4.23	4.74
$\text{Cu}_{13}(^6A_{1g})^c$	4.39	4.53	4.42	4.29	6.13
$\text{Cu}_{74}(^1A_{1g})$				—	4.76
Orbital energies for lowest 3d-like orbitals (eV)					
$\text{Cu}_1(^2S)$	12.76	12.76	12.73	12.73	—
$\text{Cu}_2(^1\Sigma_g^+)$	12.93	12.97	13.19	13.18	—
$\text{Cu}_5(^4A_2)^b$	14.24	14.37	15.09	15.04	—
$\text{Cu}_9(^2B_2)$	14.34	14.60	16.23	16.29	—
$\text{Cu}_{13}(^6A_{1g})^c$	15.02	15.32	17.76	18.03	—
Orbital energies for highest 3d-like orbitals (eV)					
$\text{Cu}_1(^2S)$	12.76	12.76	12.73	12.73	—
$\text{Cu}_2(^1\Sigma_g^+)$	12.12	12.16	12.34	12.32	—
$\text{Cu}_5(^4A_2)^b$	12.56	12.74	13.37	13.40	—
$\text{Cu}_9(^2B_2)$	12.14	12.31	13.25	13.32	—
$\text{Cu}_{13}(^6A_{1g})^c$	12.26	12.47	13.91	13.99	—

<sup>a</sup>Number of electrons per atom for the molecule in the ground state.

<sup>b</sup>The ground state is  $1a_1^2 2a_1^1 e^{24} A_2$  in all calculations.

<sup>c</sup>The ground state is  $1a_{1g}^2 2a_{1g}^1 b_{1g}^1 b_{2g}^1 e_g^2 a_{2u}^2 e_u^4 A_{1g}$  in all calculations.



from SBH<sup>7</sup> for valence orbitals; the sets used were [711/51\*/41], [711/1\*/41], [711/0/41], and [711/0/0]. The basis set for the spectral representation and the core orbitals were those used for entries e–h in Table I except for [711/0/0] where the 3*d* orbital is treated as a core and the 3*d* orbital in the shift operator of eq. (14) is that of (20/13/10).

The lowest orbital energies for the *s*- and *d*-like orbitals are given in Table V. The lowest orbital energies for the 4*s*-like orbitals of the larger clusters of Cu<sub>9</sub> and Cu<sub>13</sub> may be separated into three classes: the first is those orbital energies calculated using the basis sets {[43321/431\*/41] and [711/51\*/41]} where all the electrons or 3*p*, 3*d*, and 4*s* electrons are considered; the second is those orbital energies calculated using {[711/1\*/41] and [711/0/41]} where 3*d* and 4*s* electrons are considered; and the third is the orbital energy using [711/0/0] where only 4*s* electrons are considered. The results show that to obtain the lowest 4*s*-like orbitals properly, the 3*p* and 3*d* orbitals should be treated as valence orbitals. The orbital energy for the lowest 4*s*-like orbital of Cu<sub>13</sub> calculated using [711/0/0] is even lower than that of the lowest 3*d*-like orbital of the all-electron calculations. The highest 4*s*-like orbital energies given by the all-electron calculations and all the model-potential calculations are nearly the same for the respective clusters except for [711/0/0]. To calculate the highest 4*s*-like orbital energies properly, the 3*d* electrons must be explicitly considered. The highest and the lowest 3*d*-like orbital energies for Cu<sub>5</sub>, Cu<sub>9</sub>, and Cu<sub>13</sub> may be separated into two groups: orbital energies calculated using {[43321/431\*/41] and [711/51\*/41]} and those calculated using {[711/1\*/41] and [711/0/41]}. The latter provides orbital energies too low for 3*d*-like orbitals, indicating that the 3*p* orbitals are necessary to obtain the proper ones.

### FIRST IPs

The calculated first IPs for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, Cu<sub>13</sub>, and Cu<sub>74</sub> are summarized in Table VI together with those of the theoretical values<sup>28</sup> and experimental ones.<sup>10</sup> Except for [711/0/0], all model-potential calculations give nearly the same results as the all-electron calculations. The differences in the IPs between the all-electron calculations and [711/0/0] are consistently around 0.8 eV for Cu<sub>5</sub>, Cu<sub>9</sub>, and Cu<sub>13</sub>. By adding the correction of 0.8 eV to the [711/0/0] value for Cu<sub>74</sub>, we estimated the all-electron value of the first IP for Cu<sub>74</sub> to be 3.8 eV. When we move from Cu to

Cu<sub>74</sub>, the first IP of the all-electron calculations and that of the experimental measurement decrease by 2.5 eV. The agreement between the two is perfect. We note that the difference between the IP given by the all-electron calculation and that of experimental measurement is near constant, irrespective of the cluster size; the difference is between 1.4 and 1.8 eV.

In the Cu atom, the difference in the IPs between SCF and the experiment (1.47 eV) is nearly equal to the correlation energy between the 4*s* and the ion core of Cu (Cu<sup>+</sup>), the energy which is included in the neutral atom and not in the 4*s* electron ionized state, since the experimental IP can be expressed as

$$\begin{aligned} \text{IP (exptl)} &\approx \{\text{TE}(\text{SCF:Cu}^+) + E_{\text{corr}}(\text{Cu}^+)\} \\ &\quad - \{\text{TE}(\text{SCF:Cu}) + E_{\text{corr}}(\text{Cu}^+ \text{ core})\} \\ &\quad + E_{\text{corr}}(\text{Cu}^+ \text{ core} - 4s) \\ &= \text{IP}(\Delta\text{SCF}) + \{E_{\text{corr}}(\text{Cu}^+) - E_{\text{corr}}(\text{Cu}^+ \text{ core})\} \\ &\quad - E_{\text{corr}}(\text{Cu}^+ \text{ core} - 4s) \\ &= \text{IP}(\Delta\text{SCF}) + \Delta E_{\text{corr}}(\text{core} - 4s), \end{aligned} \quad (15)$$

where TE and  $E_{\text{corr}}$  stand for total energy and correlation energy, respectively. We may safely assume that  $E_{\text{corr}}(\text{Cu}^+) \approx E_{\text{corr}}(\text{Cu}^+ \text{ core})$ .  $\Delta E_{\text{corr}}$  is approximately written as

$$\Delta E_{\text{corr}}(\text{core} - 4s) \approx -E_{\text{corr}}(\text{Cu}^+ \text{ core} - 4s). \quad (16)$$

In the larger cluster, if one 4*s*-like electron is shared with *n* atoms that constitute the cluster, then it is reasonable to assume that the *s*–*d* correlation correction per atom is around 1/*n* of the same correlation for the Cu atom. If we deprive the cluster of one 4*s*-like electron, we may thus expect the SCF calculation will give IPs smaller than the experimental IPs at least by  $\Delta E_{\text{corr}}(\text{core} - 4s)$ , 1.47 eV, irrespective of the cluster size.

Let us discuss the correlation effects among the 4*s* shells. We write  $\Delta E_{\text{corr}}(4s - 4s)$  as

$$\begin{aligned} \Delta E_{\text{corr}}(4s - 4s) &= E_{\text{corr}}(4s \text{ for } n \text{ e}) \\ &\quad - E_{\text{corr}}(4s \text{ for } n - 1 \text{ e}). \end{aligned} \quad (17)$$

In the Cu<sub>2</sub> molecule, the IPs ( $\Delta\text{SCF}$ ) with and without  $\Delta E_{\text{corr}}(\text{core} - 4s)$  are 7.02 and 5.55 eV, respectively. The difference between the calculation and experiment is 0.35 eV for this molecule, which we attribute to the difference of the correlation energy in the 4*s* shell of Cu<sub>2</sub><sup>+</sup> and Cu<sub>2</sub>. We

**TABLE VI.**  
**Ionization Potentials by  $\Delta$ SCF with Various Numbers of Valence Electrons.**

	All Electron	Model Potentials				Correlation Corrected <sup>b</sup>	Exptl <sup>c</sup>
	29 <sup>a</sup> [43321 / 431* / 41]	17 <sup>a</sup> [711 / 51* / 41]	11 <sup>a</sup> [711 / 1* / 41]	11 <sup>a</sup> [711 / 0 / 41]	1 <sup>a</sup> [711 / 0 / 0] <sup>b</sup>		
Cu <sub>1</sub>	6.26	6.25	6.26	6.26	6.47	7.7	7.73
Cu <sub>2</sub>	5.55	5.56	5.68	5.77	5.98	7.4	7.37
Cu <sub>5</sub> <sup>d</sup>	4.52	4.62	4.71	4.78	5.38 [4.76]	6.3 [5.11]	6.30
Cu <sub>9</sub>	4.02	4.09	4.07	4.09	4.63 [3.66]	5.8 [4.12]	5.37
Cu <sub>13</sub> <sup>e</sup>	4.08	4.23	4.19	4.13	4.88	5.9	5.67
Cu <sub>74</sub>	(3.8)				4.61	(5.6)	5.26

<sup>a</sup>Number of electrons per atom for the molecule in the ground state.<sup>b</sup>The numbers in brackets are results calculated by Nygren et al.<sup>28</sup> where the 4s electrons are only treated as the real electrons and the correlations among them are given by averaged coupled pair functions.<sup>c</sup>See ref. 10.<sup>d</sup>The electron in the highest  $a_1$  orbital is ionized.<sup>e</sup>The electron in the highest  $b_{2g}$  orbital is ionized.

hereafter use 0.35 eV as the 4s correlation energy difference between the neutral molecule and the positive ion,  $\Delta E_{\text{corr}}(4s - 4s)$ . Using the effective core potentials and treating only 4s electrons as real ones, Nygren and co-workers<sup>28</sup> found that the IPs for Cu<sub>5</sub> and Cu<sub>9</sub> are 4.76 and 3.66 eV in the SCF level and 5.11 and 4.12 eV in the average coupled pair functional method (ACPF) where they performed the geometry optimization. The correlation effects increase the IP by 0.35 and 0.46 eV for Cu<sub>5</sub> and Cu<sub>9</sub>, respectively, which are near what we have estimated for the difference of the 4s correlation energy between the neutral molecule and the positive ion. Adapted correlation corrections for IP are summarized as follows:

$$\Delta E_{\text{corr}}(\text{core} - 4s) = 1.47 \text{ eV} \quad (18)$$

and

$$\Delta E_{\text{corr}}(4s - 4s) = 0.35 \text{ eV}. \quad (19)$$

The IPs of all the electron calculations with this correlation correction are given in the sixth column and experimental IPs for these clusters are given in the seventh column of figures in Table VI (rounded off to the nearest tenth eV). The correspondence between the two is excellent; the difference in IPs between the calculations and experiments, however, is a little larger for the large clusters, indicating that the geometry optimization might be necessary for these clusters as Nygren and coworkers found.<sup>28</sup>

## EAs

The EAs for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, Cu<sub>13</sub>, and Cu<sub>74</sub> are presented in Table VII together with those of Åkeby et al.<sup>29</sup> The results of the model-potential calculations done using [711/51\*/41] closely approximated those of the all-electron calculations.

With Cu<sub>13</sub>, the all-electron [43321/431\*/41] calculation and model-potential {[711/51\*/41], [711/1\*/41], and [711/0/41]} calculations give EAs of the same magnitude. For Cu<sub>13</sub>, [711/0/0] gives an EA of 1.90 eV, larger than that of the all-electron calculation by 1 eV. We have estimated that the all-electron calculation gives an EA of 1.6 eV for Cu<sub>74</sub>, subtracting 1 eV from the EA of [711/0/0]. Applying the correlation correction of 1.82 eV [sum of eqs. (18) and (19)] to the EA of the all-electron calculations, we give a correlation corrected EA of 3.4 eV in Table VII. The correlation corrected EA for the respective clusters always shows good agreement with the experimental EA with the sole exception of Cu<sub>2</sub>. The EA for Cu<sub>2</sub> is calculated not at the equilibrium bond distance but at the bond distance of the nearest neighbor in the solid. We recalculated the EA at the equilibrium bond distance of 4.19 au and obtained an EA of -0.45 eV by the all-electron SCF calculation. The EA with the correlation correction was calculated to be 1.35 eV, which is still much larger than the experimental value of 0.88 eV. We note that an augmented electron is in a rather diffuse antibonding orbital and the correlation effects among this and other electrons are expected to be smaller than those given in eqs. (18) and (19). Åkeby and col-

**TABLE VII.**  
**Electron Affinity by  $\Delta$ SCF with Various Numbers of Valence Electrons.**

	All Electron	Model Potentials				Correlation Corrected <sup>b</sup>	Exptl
	29 <sup>a</sup> [43321 / 431* / 41]	17 <sup>a</sup> [711 / 51* / 41]	11 <sup>a</sup> [711 / 1* / 41]	11 <sup>a</sup> [711 / 0 / 41]	1 <sup>a</sup> [711 / 0 / 0]		
Cu <sub>1</sub>	-0.36	-0.33	-0.33	-0.33	-0.25	1.5 [0.75]	1.26 <sup>c</sup>
Cu <sub>2</sub>	-0.24	-0.18	-0.16	-0.16	0.10	1.6 [0.69]	0.88 <sup>d</sup>
Cu <sub>5</sub> <sup>e</sup>	0.22	0.36	0.62	0.58	1.16	2.0 [1.63]	1.94 <sup>d</sup>
Cu <sub>9</sub> <sup>f</sup>	0.27	0.39	0.50	0.40	1.57	2.1 [2.17]	2.40 <sup>d</sup>
Cu <sub>13</sub> <sup>g</sup>	0.92	1.28	1.27	1.17	1.90	2.7	2.74 <sup>c</sup>
Cu <sub>74</sub>	(1.6)				2.62	(3.4)	3.0–3.3 <sup>c</sup>

<sup>a</sup>Number of electrons per atom for the molecule in the ground state.<sup>b</sup>The numbers in brackets are results calculated by Åkeby and co-workers<sup>29</sup> where the 4s electrons are only treated as the real electrons and the correlations among them are given by externally contracted CI levels including Davidson's correction. The correlation effects between the 3d and 4s electrons are included through the use of the approximate core polarization potentials.<sup>c</sup>See ref. 12.<sup>d</sup>See ref. 11.<sup>e</sup>The augmented electron enters the highest occupied e orbital of the ground state ( $1a_1^2 2a_1^1 e^2$ ).<sup>f</sup>The augmented electron enters the highest half-occupied  $b_{2g}$  orbital.<sup>g</sup>The augmented electron enters the lowest unoccupied  $a_{1g}$  orbital of the ground state ( $1a_{1g}^2 2a_{1g}^1 b_{1g}^1 b_{2g}^2 e_g^2 a_{2u}^2 e_u^4$ ).

leagues<sup>29</sup> gave a realistic value of 0.69 eV. Since the difference in the correlation correction among the valence electrons becomes constant for the larger clusters, the correlation corrected EAs are expected to be better for larger clusters. The agreement between the experimental and correlation corrected EAs for Cu<sub>13</sub> and Cu<sub>74</sub> support this argument.

## Concluding Remarks

We investigated the characteristics of a spectral-representation model potential method. We have seen that to calculate the lowest orbital energy of the 4s-like orbitals properly, we should treat the 3p-, 3d-, and 4s-like orbitals as valence orbitals. The highest orbital energy of the 4s-like orbitals is properly described when the 3d- and 4s-like orbitals are treated as valence orbitals. To calculate the orbital energy distributions of the d-like orbitals, it is necessary to add 3p orbitals to the valence orbitals.

The calculated first IPs from the SCF approximation are 6.3, 5.6, 4.5, 4.0, 4.1, and 3.8 eV for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, Cu<sub>13</sub>, and Cu<sub>74</sub>, respectively; the IPs calculated adding the correlation correction are 7.7, 7.4, 6.3, 5.8, 5.9, and 5.6 eV. The experimental IPs for these clusters are 7.7, 7.4, 6.3, 5.4, 5.7, and 5.3 eV, showing good agreement with the theoretical calculations. EAs calculated adding the correlation corrections are 1.5, 1.6, 2.0, 2.1, 2.7, and 3.4 eV

for Cu, Cu<sub>2</sub>, Cu<sub>5</sub>, Cu<sub>9</sub>, Cu<sub>13</sub>, and Cu<sub>74</sub>, respectively; the experimental EAs are 1.3, 0.9, 1.9, 2.4, 2.7, and 3.0–3.3 eV. We used the same correlation correction when we calculated the IPs and EAs. The correlation correction adapted for EAs is too large when the augmented electron in the negative ion broadens the half-occupied orbital of the ground state, as in case of the Cu atom, or the augmented electron enters into the diffuse anti-bonding orbital (Cu<sub>2</sub>).

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